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Synthetic Organic Chemicals

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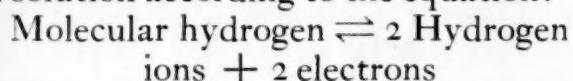
VOL. II

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No. 1

The Quinhydrone Electrode

THE hydrogen electrode has long been the accepted means of determining the acidity and basicity of solutions. Its use is based on the tendency for molecular hydrogen (surrounding a platinum black electrode) to furnish hydrogen ions in solution according to the equation:



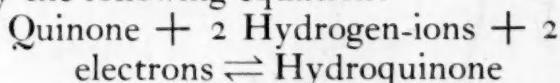
When the conditions of the molecular hydrogen are fixed as to temperature, pressure, etc., the potential drop depends only on the hydrogen-ion concentration. The E.M.F. of this electrode opposed to some complementary standard electrode can be measured by a potentiometer, and from this value the hydrogen-ion concentration can be calculated. The immense amount of study that has been given to the theory and use of the hydrogen electrode makes it still the standard for extremely accurate work. It does, however, have many disadvantages, some of which are not encountered in using the quinhydrone electrode.

With the hydrogen electrode, the platinum strip must be blackened by a special treatment in order to make it suitable for the work. This platinum black is susceptible to "poisoning" and in addition sometimes acts as a catalyst promoting reactions which interfere with the determination. The activity of the hydrogen as a reducing agent often pre-

vents its use, especially with oxidizing agents and unsaturated organic compounds. Since the electrode must be saturated with hydrogen at all times, a continuous stream of the gas is kept bubbling through the liquid. This removes volatile compounds or dissolved gases if present, thus altering the composition of the solution. Much time is often required for the platinum black to become saturated with the gas and to come to equilibrium.

Since the quinhydrone electrode has none of these troubles, it has claimed the attention of many able scientists in the last few years. Probably the greatest amount of work has been done on this subject by Professor Einar Biilmann and his co-workers at the University of Copenhagen.

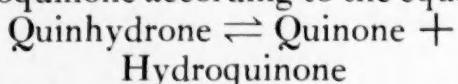
When quinone and its reduction product, hydroquinone, are present in the solution, the equilibrium may be expressed by the following equation:



An electro-potential is therefore set up whose value depends on the concentration of quinone, the concentration of hydroquinone, and the hydrogen-ion concentration. If the concentrations of the quinone and hydroquinone could be kept constant, this potential would depend entirely on the concentration of

hydrogen-ions. This desirable condition can be attained by the use of quinhydrone.

Quinhydrone, or more specifically, benzoquinhydrone dissociates in solution to equivalent amounts of quinone and hydroquinone according to the equation:



The amount of quinhydrone used for the electrode has no influence since the quinone and hydroquinone are always formed in equivalent amounts. The solubility of quinhydrone is so slight that the usual practice is to add an excess of the crystals to form a saturated solution in the liquid to be examined.

The electrode most commonly used for hydrogen-ion determinations is extremely simple, consisting merely of a piece of platinum foil immersed in a beaker containing the solution under examination which has been saturated with crystals of quinhydrone. The customary potassium chloride bridge is used to connect this solution with a calomel or other half-cell, and the potential difference between the two terminals measured by a potentiometer. From this value, the hydrogen-ion concentration or pH value can be readily calculated.

Owing to its simplicity, the quinhydrone electrode has found many practical applications, a few of which may be mentioned here. Many organic compounds which would be reduced by a hydrogen electrode, can be studied by the use of the quinhydrone electrode. It is possible to obtain pH values for acrylic, fumaric, phenylpropionic, chloroacetic and iodopropionic acids, all of which are reduced by hydrogen in the presence of platinum black. The hydrogen-ion concentration of blood may also be quite easily determined since no special precautions are necessary to prevent the escape of carbon dioxide as is the case when hydrogen gas must be bubbled through.

In connection with the application of

the quinhydrone electrode to blood and other biological products, capillary electrodes have been devised which require only a few drops of material. One form consists of a capillary tube or pipette containing a movable platinum wire. After dipping the end of the wire in powdered quinhydrone, it is pulled back inside of the tube and a small amount of the liquid under examination is drawn up into the pipette. The circuit to the calomel half-cell is completed by dipping the end of the pipette into the salt bridge between the two electrodes.

The rapidity of the quinhydrone electrode in coming to equilibrium is a real advantage since in most cases the pH values can be determined within two or three minutes. This not only permits speeding up the number of determinations but also allows readings to be made on solutions which react slowly with the quinone or hydroquinone. With dilute nitric acid, for instance, the initial potential is reached so quickly that several reproducible values are obtained before the quinone-hydroquinone ratio is altered.

Much work has been done with quinhydrone in the analysis of soils. Over 50,000 soil acidity determinations have been made in one laboratory alone. In this particular instance it was found convenient to replace the complementary calomel electrode by another quinhydrone electrode in which the pH was fixed by a buffer solution. The quinhydrone electrode is also used to determine the acidity of milk, cheese, butter, etc. Other applications include pH measurements of gastric sugars, urine, alkaloids, and proteins.

There are some disadvantages in the use of the quinhydrone electrode which must also be considered. It cannot be used satisfactorily in solutions more alkaline than pH 8. Under these conditions hydroquinone dissociates like a very weak acid and also becomes more susceptible to oxidation by air. The

quinhydrone-hydroquinone ratio is thus altered so that the hydrogen-ion concentration no longer bears the same relation to the potentiometer reading. As with the hydrogen electrode, strong oxidizing and reducing agents interfere with the equilibrium conditions. As explained above, the concentrations of quinone and hydroquinone are kept constant by the dissociation of the quinhydrone. However, in relatively concentrated solutions, the solute may affect the relative activities of the two components. In di-

lute solution, this "salt effect" may be ignored, but in solutions more concentrated than fifth-molar, a correcting factor must be applied.

Very similar to the quinhydrone electrode is the chloranil electrode which has been studied recently by Dr. J. B. Conant at Harvard. The oxidizing and reducing agents in this case are tetrachloroquinone (chloranil) and tetrachlorohydroquinone. Its principal application so far has been in the study of hydrogen-ion concentrations in nonaqueous solutions.

A Constant Temperature Bath

The organic chemist frequently has occasion for a constant temperature bath, accurate within a few tenths of a degree, which can be readily installed and as readily replaced on the shelf when it has served its purpose. Such an apparatus must be of simple and rugged construction and afford temperatures over a wide range.

These conditions, it is believed, are met by the device here depicted (Fig. 1), consisting of a bath surrounded by the vapor of a definite liquid or constant-boiling mixture of liquids. Small sizes may readily be constructed from copper glue-pots, by soldering the inner member to the outer, and tubulating the upper portion of the jacket for the attachment of a reflux condenser. Larger sizes, and those required for temperatures above 150°C , are best constructed in a sheet-metal shop, of welded black iron plate.

The bath may consist, for temperatures below 100° , of water, covered with a thin layer of lubricating oil to prevent evaporation. For higher temperatures, machine or medicinal oils are suitable. The apparatus, if suitably covered, also

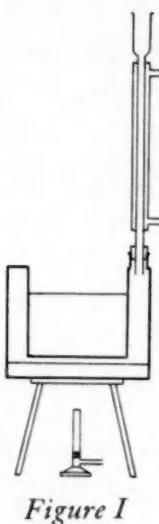


Figure I

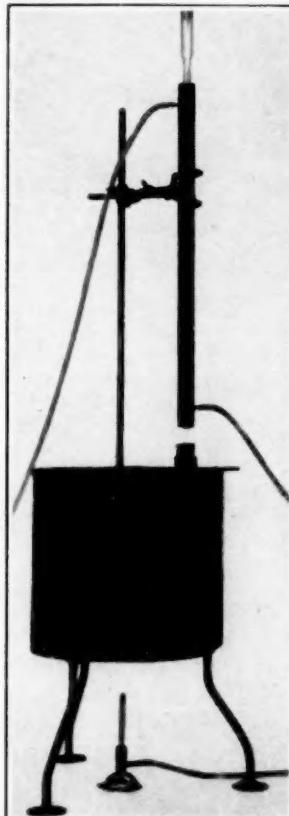


Figure II

forms a convenient air-bath as shown by the accompanying photograph.

The following suggestions are offered for liquids in the vapor jacket:

- 35° Ethyl Ether
- 42° Methylal
- 56° Acetone
- 64° Methyl Alcohol
- 69° Benzene — water (azeotropic mixture)
- 78° Ethyl Alcohol
- 84° Ethylene Chloride
- 92° Butyl Alcohol — water (azeotropic mixture)
- 100° Water
- 110° Toluene
- 116° Butyl Alcohol
- 126° Butyl Acetate
- 132° Chlorobenzene
- 139° Iso-Amyl Acetate
- 157° Bromobenzene
- 165° Butyl Butyrate
- 175° Cymene
- 183° Aniline
- 193° Dimethylaniline
- 206° Tetrahydronaphthalene

Organic Chemicals as Analytical Reagents

VI REAGENTS FOR IRON

CUPFERRON

Baudisch and King, Ind. and Eng. Chem. 3, 629 (1911)

Iron and copper are precipitated from acid solutions by this reagent. By washing the precipitate with dilute ammonia the copper compound dissolves, leaving the insoluble iron salt on the filter. The sample is dissolved in concentrated hydrochloric acid, oxidized with potassium chlorate and, after expelling the chlorine, diluted with distilled water. The reagent (3 gm. of cupferron in 50 cc. water) is added with stirring, giving a brownish red precipitate. A white crystalline precipitate appears when all of the iron is out of the solution. After washing with water and dilute ammonia the precipitate is ignited and weighed as Fe_2O_3 .

DIMETHYLGLYOXIME

Tschugaeff and Orelkin, Z. Anorg. Chemie. 89, 401 (1914)

A solution containing ferrous-iron is colored a deep red when a solution of dimethylglyoxime is added. Ferric-iron, which does not give the test, can be easily reduced quantitatively by hydrazine sulfate. Fifty cc. of the solution to be examined is treated with 1 gm. of hydrazine sulfate and 5 cc. of a saturated alcoholic dimethylglyoxime solution and then heated to boiling. Twenty-five cc. of 25% ammonia is then added, continuing the boiling for 0.5 minute. After cooling, it is diluted to 100 cc. and compared in a colorimeter with a standard iron solution similarly treated.

Iso-NITROSOACETOPHENONE

F. Krohnke in Berichte, 60, 527 (1927)

This reagent is employed in the form of a decinormal solution in chloroform. The dilute, neutral solution of ferrous

salt is treated with 1 cc. of the reagent and 1 cc. of decinormal ammonia. As little as 0.03 mg. of ferrous iron per liter gives a blue chloroform layer.

ACETYLACETONE

Pulsifer, J. A. C. S., 26, 967 (1904)

Three-millionths of a gram of iron in 50 cc. of water will give a distinct red color when treated with a $\frac{1}{2}\%$ solution of acetylacetone. The depth of color in such solutions is proportional to the amount of iron present, within the limits of 0.000003 g. to 0.0006 g. Most of the other inorganic salts cause no interference even in amounts as large as 0.2 gram.

SALICYLIC ACID

Gregory, J. C. S., 93, 93 (1908)

Salicylic acid gives a violet coloration to iron solutions, changing to a deep red when sodium acetate is added. To the ferric-iron solution 20 cc. of a concentrated sodium acetate solution is added and then 10 cc. of 2% salicylic acid in glacial acetic acid. If copper is present, the green color may be removed by the addition of a few drops of 3% potassium cyanide. The solution is diluted up to a definite volume and the red color compared with that of a known iron solution which has had the same treatment.

New Chemicals

The following preparations have become available during the summer.

- *Acetyl Piperidine (Pract.)
- *n-Amyl Acetate
- *n-Amyl n-Butyrate
- *n-Amyl Propionate
- *Bromopicrin
- *Carvoxime
- *Cysteine Hydrochloride
- * α - β -Dibromoethylene
- *p,p'-Dihydroxydiphenyl
- Ethylene glycol Monomethyl Ether (Pract.)
- Magnesium Perchlorate (Anhydrous)
- *Made or purified in the Kodak Research Laboratories.